Low temperature specific heat of the heavy fermion superconductor $PrOs_4Sb_{12}$

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(February 1, 2008)

We report the magnetic field dependence of the low temperature specific heat of single crystals of the first Pr-based heavy fermion superconductor $PrOs_4Sb_{12}$. The low temperature specific heat and the magnetic phase diagram inferred from specific heat, resistivity and magnetisation provide compelling evidence of a doublet ground state and hence superconductivity mediated by quadrupolar fluctuations. This establishes $PrOs_4Sb_{12}$ as a very strong contender of superconductive pairing that is neither electron-phonon nor magnetically mediated.

PACS numbers: 74.70.Tx, 65.40.-b, 7127,+a, 75.30.Mb

Superconductivity mediated by a pairing potential other than a conventional electron-phonon interaction has been the subject of a very large number of theoretical and experimental investigations over the decades. In recent years, finally, intermetallic compounds have been discovered which, together with the high-T_c cuprates, represent prime candidates for magnetically mediated pairing. Surprisingly, however, magnetically mediated pairing thus far has been considered the only serious alternative to electron-phonon mediated pairing, while excitonic and polaronic mechanisms have also been proposed.

We have recently reported the discovery of the first Pr-based heavy fermion superconductor $PrOs_4Sb_{12}$ [1], for which the nonmagnetic ground state appeared best described as a crystalline electric field (CEF) doublet. This in turn suggested that the heavy electron liquid is of quadrupolar origin and that consequently quadrupolar fluctuations mediate the superconductive pairing. $PrOs_4Sb_{12}$ hence is a candidate for being the first material in which neither electron-phonon nor magnetic interactions mediate the pairing. However, a magnetic origin could not be completely ruled out [1] and recent low temperature specific heat measurements are reported to be consistent with a singlet CEF ground state hence questioning the hypothesis of quadrupolar pairing [2].

In order to settle the question of the ground state and thus the possibility of the first example of quadrupolar mediated superconductive pairing demands definitive establishement of (i) the CEF level scheme, (ii) the unconventional nature of the superconductivity, and (iii) coupling of the CEF excitations to the conduction electrons. Here we report specific heat measurements of high quality single crystals of $PrOs_4Sb_{12}$ at low T and high magnetic field. We show that the zero field data of the single crystals and the magnetic phase diagram as established from the specific heat, resistivity and magnetisation, as well as the observation of a novel high field ground state, provide compelling evidence of a nonmagnetic doublet CEF ground state intimately linked to the conduction electrons. This unambiguously establishes quadrupolar fluctuations as the most likely pairing mechanism. Moreover, we observe two superconducting transitions giving evidence of two distinct superconducting phases.

Previous experiments on pressed pellets of tiny single crystals of $PrOs_4Sb_{12}$ [1] revealed superconductivity at $T_c = 1.85$K with an upper critical field $B_{c2}(T \to 0) =$ 2.5 T. The superconductivity appears to involve heavy quasiparticles with an effective mass $m^* \approx\ 50\ m_e$ as inferred from the jump in the specific heat at T_c, the slope of the upper critical field B_{c2} near T_c, and the normal state electronic specific heat.

The normal state properties of $PrOs_4Sb_{12}$ exhibit features with a single dominant energy scale of order several K. The low field uniform susceptibility indicates a nonmagnetic groundstate, characterised by a maximum at 3 K and an enhanced zero temperature susceptibility of 0.06 cm^3/mol. Well above the maximum a Curie–Weiss law is observed with an effective moment of $\mu_{eff} = 2.97\mu_B$ and a Curie–Weiss temperature $\Theta_{\rm CW} = -16$K. The electrical resistivity drops monotonically from room temperature to T_c by nearly two orders of magnitude and displays a shoulder at a temperature of order 7 K, below which a very weak T^2 temperature dependence is observed. Finally, the normal state specific heat displays a Schottky anomaly with a peak at $T^* = 2.1$ K. These data [1] were shown to be consistent with a Γ_3 doublet ground state and Γ_5(11K), Γ_4(130K) and Γ_1(313K) excited states, suggesting a quadrupolar origin of the heavy electron liquid. Nevertheless, a Γ_1 singlet ground state and Γ_5(6K), Γ_4(65K) and Γ_3(111K) excited states could not be ruled out.

Preliminary studies [3] of the low lying excitations by inelastic neutron scattering (INS) confirm the presence of a CEF level at 0.71 meV (8.2 K) and 11.5 meV (133 K) in excellent agreement with previous assignments of a Γ_3

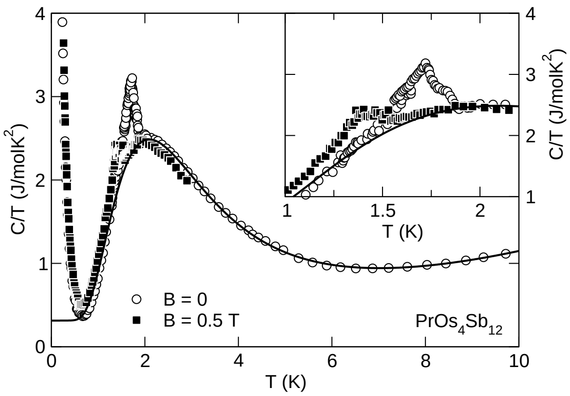

FIG. 1. Specific heat C/T vs. temperature T in magnetic fields $B \parallel \langle 100 \rangle$ up to 0.5 T. The inset displays the specific heat near the superconducting transition, where the double transition can no longer be resolved at 0.5 T.

ground state. Further evidence for such a ground state is also provided by recent non-linear susceptibility measurements [4]. Transverse-field muon spin relaxation of the superconducting flux line lattice shows the absence of nodal structure [5] expected for a magnetically mediated superconducting state, and is also consistent with a quadrupolar origin of the superconductivity [6].

The high quality single crystals of $PrOs_4Sb_{12}$ grown from Sb flux [7], have very narrow superconducting transitions in both resistivity and susceptibility and a low residual resistivity $\rho_0 < 5\mu\Omega$cm. The samples naturally crystallized in a cubic shape, where the principal crystallographic axis were confirmed to coincide with faces of the cubes by means of Laue x-ray diffraction. Powder x-ray diffraction using a careful Rietveld analysis showed that the samples were single phase with the correct Pr occupancy [8]. Occasional minor impurity phases were identified to be elemental Sb and Os in n-scattering studies [3]. Recently, de Haas–van Alphen oscillations were observed in single crystal samples from the same growth, providing evidence of long charge carrier mean free paths [9].

In previous studies of pressed pellets of tiny single crystals [1], C was found to be reduced by up to 50% due to inclusions of Sb flux. In the present work we measured the specific heat of an aggregate of five small single crystal pieces ($\sim$ 10mg) all showing very well developed facets. The results were compared, where necessary, with the specific heat of a large single crystal ($\sim$ 3.55 mg). The aggregate of five single crystals displayed the highest specific heat thus far reported, while that of the single piece is reduced by 9% indicating a small quantity of Sb inclusions. We find that T^* and T_c are sample independent. Moreover, we always find two distinct superconducting transitions.

The specific heat was measured with a quasi-adiabatic heat pulse technique in a ^{4}He cryostat down to 1.5 K in magnetic fields up to 14 T [10] and in a dilution refrigerator down to 100 mK in magnetic fields up to 6.65 T [11]. Magnetic fields were applied along the principal cubic axis. We observe an excellent quantitative agreement to better than a few per cent in the temperature and field range of overlap between the two experimental set ups, which employ different thermometers and sample holders. We note that the specific heat of materials with large, weakly coupled nuclear contributions as for $PrOs_4Sb_{12}$ display quasiadiabatic thermal relaxation times that easily exceed several minutes. Using a very low noise resistance bridge and automated detection electronics we were able to keep track of these extremely slow relaxation processes. Our results distinctly differ from recent work reported in reference [2]. However, we do observe data consistent with those reported in [2] when evaluating our data using the initial T versus time dependence following a heat pulse, for which nuclear contributions are still decoupled.

Shown in Fig. 1 is the specific heat plotted as C/T versus T for low magnetic fields. With decreasing temperature, C/T exhibits the well-established maximum at $T^* \approx 2.1$ K, decreases again to lower temperatures, followed by a very pronounced upturn at the lowest T. The superconducting transition at $T_c \approx 1.85$ K is accompanied by a well developed anomaly in the specific heat.

We focus first on the normal state specific heat. For $B = 0$ and $T > T_c$ up to 10 K, C/T may be well described as a sum of three contributions (solid line): (i) an electronic part $C/T = \gamma = 313$ mJ/molK^2, (ii) a phononic (cubic) part with a characteristic temperature of $\Theta = 165$ K and (iii) a Schottky anomaly due to CEF splitting of the Pr $^3H_4$ ground state to a Γ_3 ground state doublet and Γ_5 triplet with an energy separation of $\Delta = 7.0$ K.

In comparison to previous work we find a slightly reduced value of γ. This may be related to higher sample quality and/or the different account of the lattice contribution, which was previously taken as the lattice specific heat of $LaOs_4Sb_{12}$ ($\Theta_D = 304$ K). We did not use the lattice specific heat of $LaOs_4Sb_{12}$ here, because the lanthanide contraction suggests softer phononic rattling modes for the Pr compound than for the La compound consistent with the value of the characteristic temperature $\Theta = 165$ K.

We have carefully fitted various CEF schemes for the Schottky anomaly [11]. Δ can be unambiguously determined from T^* of the Schottky anomaly and is thus not a free fit parameter. In contrast, the absolute height of the anomaly depends sensitively on the number of Pr ions per formula unit and the degeneracy of the levels involved. The data may only be accounted for by the Γ_3 doublet ground state and a Γ_5 triplet excited state, where $\Delta = 7.0$ K corresponds very well with the INS data [3] and the prefactor is precisely 1 Pr/f.u.. For other level splitting schemes the difference is in excess of a factor of two. This fully confirms the level scheme originally pro-

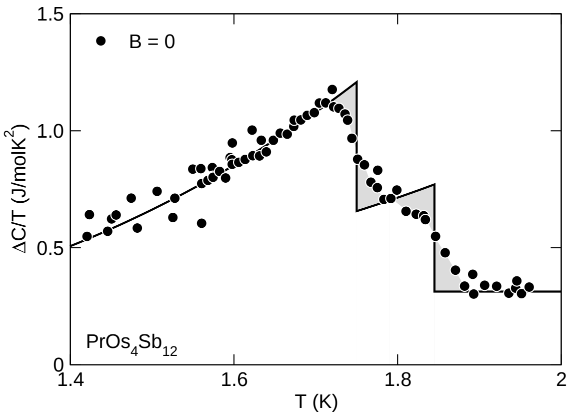

FIG. 2. Electronic contribution to the specific heat $\Delta C/T$ vs. temperature T. The solid curve shows an entropy conserving construction as explained in the text.

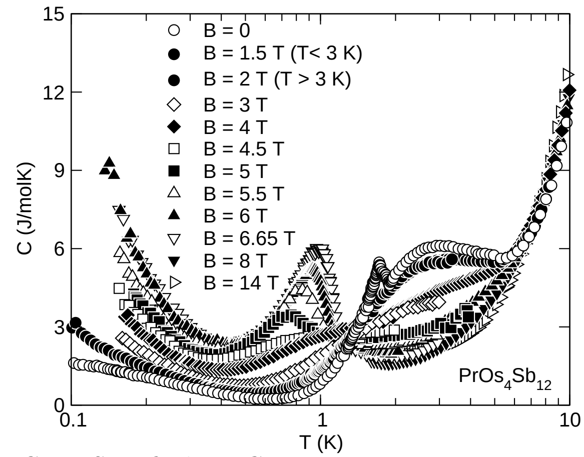

FIG. 3. Specific heat C vs. temperature T in magnetic fields $B \parallel \langle 100 \rangle$ up to 14 T. The high T Schottky anomaly is rapidly suppressed up to 14 T. A pronounced anomaly, indicating an ordered state stabilized in high field, is resolved at low T.

posed in [1]. We also note that the electronic and lattice contributions up to 10 K are essentially negligible.

Evidence for unconventional superconductivity may be seen in the specific heat anomaly (Fig. 1) in terms of two pronounced anomalies, where the upper transition coincides with the zero resistance and Meissner transition temperature. The double transition has been observed in the aggregate of five small single crystals and also the large single piece. It is present in all single crystalline samples studied to date, apart from the pressed pellets [1], which display a broad hump at the superconducting transition. In all cases for which the double transition is seen, the transition temperatures and the size of the superconducting anomalies are in very good *quantitative* agreement. This clearly rules out sample inhomogenities as a possible cause. We further note that the double transition is also seen in the thermal expansion of single crystals [12].

The specific heat for $B = 0$ near T_c after subtraction of the phonon and the Schottky contributions is shown as $\Delta C/T$ vs. T in figure 2. The solid line represents an equal entropy construction showing that the two transitions are of equal height. The two superconducting transition temperatures are estimated to be $T_{c1} = 1.75$ K and $T_{c2} = 1.85$ K. The ratio $\Delta C_{sc}/\gamma T_c \approx 3$, where ΔC_{sc} is the total height of both superconducting jumps taken together. It exceeds the weak coupling BCS value $\Delta C_{sc}/\gamma T_c = 1.43$. Secondly, the entropy of the total superconducting anomaly compares with that of the normal state as expected [11].

The two superconducting transitions are reminiscent of the only other stoichiometric metal exhibiting this type of behaviour, UPt_3, which displays a complex superconducting phase diagram as a function of magnetic field [13] and pressure [14]. We find that the double transition in $PrOs_4Sb_{12}$ may no longer be resolved in 0.5 T, making more measurements necessary to establish the fate of the double transition in magnetic field.

The specific heat C as a function of T in high magnetic fields up to 14 T is shown in Fig. 3. Data above 6.65 T could only be measured above 1.5 K. The Schottky anomaly is strongly suppressed by the magnetic field. For $T \to 0$ a strong increase of C is observed. Above 2 T, data were not taken below 0.16 K because the weakly coupled, very large nuclear contributions could no longer be accounted for as explained above. The low T increase is consistent with the splitting of the Γ_3 doublet ground state in a magnetic field and additional contributions from hyperfine enhanced Zeeman splitting of the Pr nuclear levels. The observed behaviour exceeds by a large margin that reported in reference [2] and clearly refutes the main argument presented in that paper supporting a singlet ground state.

The Zeeman splitting of the Γ_3 doublet and Γ_5 triplet CEF levels is shown in figure 4. Here the upper doublet and the lowest triplet level cross at $B = 4.5$ T suggesting a possible change of ground state at this field. Indeed, the low temperature specific heat at high magnetic fields displays a pronounced maximum for $B > 4.5$ T that shifts from $T = 0.7$ K for $B = 5$ T to $T = 1$ K for $B = 6.65$ T and sharpens considerably. This shows the stabilisation of a new thermodynamic ground state at high magnetic field, driven by the Zeeman split level crossing of the Γ_3 doublet and Γ_5 triplet CEF. A change of ground state is also evident from two crossing points common to the $C(T)$ curves [15], one below and one above 4 T, in line with two fundamentally different ground states. A quantitative account of the high field specific heat is beyond the present work, since the hybridisation of the f-electrons with the conduction electrons can not be fully acocunted for. The existence of the high field phase nevertheless fully confirms the first excited CEF triplet at $\Delta = 7.0$ K and is consistent with the ground state dou-

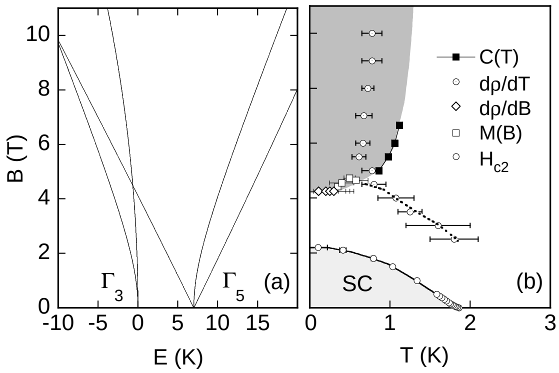

FIG. 4. (a) Zeeman splitting of the Γ_3 doublet and Γ_5 triplet CEF levels used for fitting the zero field specific heat. The doublet and triplet cross at about 4.5 T, suggesting a stabilisation of a different ground state at high field. (b) Magnetic phase diagram deduced from the specific heat C, magnetisation M and derivative of the resistivity $d\rho/dT$ and $d\rho/dB$. The high field phase is clearly driven by the level crossing due to the Zeeman splitting. The zero field energy scale evident in all properties is clearly connected with the Pr^{3+} Γ_3 - Γ_5 level splitting.

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The interplay of the CEF excitations with the conduction electrons is readily evident from kinks at low fields and maxima at high fields in the derivatives of the resistivity $d\rho/dT$ and $d\rho/dB$, calculated from the raw data, and low T magnetisation [8]. When combining these features with the sharp anomaly in the specific heat a unified phase diagram shown in figure 4 (b) may be constructed that also agrees with features of the magnetisation. In this phase diagram at low fields the maxima track the calculated Zeeman splitting of the Γ_3 and the lowest Γ_5 level. This provides a natural explanation for the energy scale of a few K at zero field seen in the resistivity, susceptibility and specific heat. Moreover, the very low Kadowaki-Woods ratio A/γ^2 just above T_c at zero field [1,3] (A is the coefficient of T^2 contribution to the resistivity), is boosted to a conventional value for $T \rightarrow 0$ in a magnetic field above ~ 4 T. Thus the CEF sensitively affects the properties of the conduction electrons, even at high magnetic fields.

The origin of the high field phase and its consistency with the doublet ground state may be reminiscent of the properties of $PrPb_3$ [16] and $PrFe_4Sb_{12}$ [17], both of which stabilise antiferroquadrupolar order (AFQO) at low temperatures by virtue of a Jahn-Teller distortion. For $PrPb_3$, the ordering temperature T_{AFQO} is shifted to higher values in magnetic field before it collapses to zero above ~ 7 T [11], in qualitative agreement with the increase of the onset of the high field phase in $PrOs_4Sb_{12}$. The magnetic field dependence in $PrPb_3$ is thereby driven by the Zeeman splitting of the CEF. Although $PrPb_3$ has a Γ_3 doublet ground state and the first excited state is a Γ_4 and not Γ_5 triplet, as for $PrOs_4Sb_{12}$, AFQO at high fields is a real possibility. A possible suppression of the high field state and qualitative analogy of the magnetic phase diagram with that of $PrPb_3$ may therefore already provide compelling evidence of AFQO in magnetic fields in $PrOs_4Sb_{12}$, where neutron scattering experiments at high field are required for final proof.

In conclusion we have examined the specific heat of single crystalline $PrOs_4Sb_{12}$ and found the data up to 10 K and in high magnetic field well explained by a Γ_3 doublet ground state and Γ_5 excited state, consistent with the previous specific heat in zero field on pressed pellets [1]. We observe a double superconducting transition indicating two distinct superconducting phases, thereby highlighting the unconventional nature of the superconductivity. At high magnetic field, we find that a novel groundstate is stabilised in magnetic field. The magnetic phase diagram may tracked also by features of the electrical resistivity. Since the Zeeman splitting also removes fluctuations related to the degeneracy of the doublet groundstate, these are likely to be instrumental to the superconductive pair formation. When taken together, the evidence presented here establishes $PrOs_4Sb_{12}$ as very strong contender for quadrupolar superconductive pairing, i.e., neither electron-phonon nor magnetically mediated.

Financial support by the Deutsche Forschungsgemeinschaft, U.S. National Science Foundation, U.S. Departement of Energy and Alexander von Humboldt Stiftung and help during the experiments by G. Linker and F. Obermair are gratefully acknowledged.

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